Demonstration and Commercialization of ARoNite™, A Novel Hydrogen-based Membrane Biofilm Biological Reduction Process

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What is Denitrification Using Hydrogen?

 Denitrification is a dissimilatory biological process that sequentially reduces NO₃⁻ to N₂

$$NO_3^- + 2e^- --> NO_2^-$$

 $+ e^- --> NO$
 $+ e^- --> 0.5N_2O$
 $+ e^- --> 0.5N_2$

We chose H₂ gas as the electron donor

$$H_2 --> 2H^+ + 2e^-$$



What are the proper conditions?

- Anoxia, or dissolved oxygen removed
- Excellent biomass retention, usually as a biofilm
- Satisfactory pH, near neutral
- Availability of nutrients, particularly P
- Sufficient electron donor
 - Organic compound (for heterotrophs)
 - Hydrogen gas (H₂) (for autotrophs)





Why Bacterial Reduction Using Hydrogen?

Major advantages over organic e- donors (heterotrophic)

- H₂ supports <u>autotrophic bacteria</u>, which use bicarbonate as their Carbon source; thus, <u>no organic Carbon source must be added</u>.
- Relatively low-cost electron donor that is commercially available as a bulk chemical <u>or can be generated on-site</u>.
- No dosing challenge, easy to control
- Non-toxic, no residual
- Low biomass yield, producing less biomass that must be wasted.
- Based on growing microbiology research, H₂ should be available as donor for virtually <u>all oxidized contaminants</u>.



What is at the core of the process?

- A novel natural partnership between technology and biofilms.
- For the first time, we can deliver H₂ to microorganisms as the electron donor in a safe and efficient manner.
 - Gaining all those advantages discussed in previous slide!



ARoNite (MBfR) Brief History

- Membrane Biofilm Reactor Concept ~ 1996 by Dr. Bruce Rittmann & Dr. K-C Lee
- Demonstration for denitrification (late 1990s) –Dr. Rittmann & Dr. Lee
- First publication (2000); now > 40 publications
- Demonstration for perchlorate reduction (early 2000s) -- Dr. Rittmann & Dr. Lee
- Field demonstration (early 2000s) w/ MWH
- First patent (2002)
- APTwater licenses the technology and partners (2004)
- Since 2005 APTwater has been expanding the scope of oxidized contaminants, conducting field testing, developing commercial system
- The concept was awarded the 2011 Environmental Engineering Excellence Award from the American Academy of Environmental Engineers!
- ARoNite received NSF 61 certification in Dec 2011
- The first commercial ARoNite system went on line in Jan 2012
- CDPH testing and review 2012
- ARoNite will be the one of the first permitted and operating biological reduction process in the US for drinking water treatment



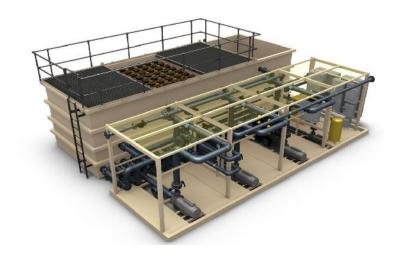
What does ARoNite stand for?

ARo Technologies –

<u>Autotrophic</u> — an organism capable of making organic molecules from inorganic sources. Examples are plants, algae, some bacteria

Reduction — Chemical reaction in which an electron is gained

<u>of</u> - Nitrates, Chromium, Selenium and other compounds



Targeting <u>Autotrophic</u> <u>Reduction</u> <u>of</u> <u>Nitrates to innocuous compounds, using hydrogen, carbon dioxide and electricity as consumables.</u>

In development testing are:

- •ARoChrome targeting Cr⁶⁺ in water supplies
- •ARoPerc targeting specific chlorinated compounds in water i.e. ClO4
- •ARoSel targeting Selenium, naturally occurring and from flue gas desulfurization, oil production and refining



How the ARoNite System Works

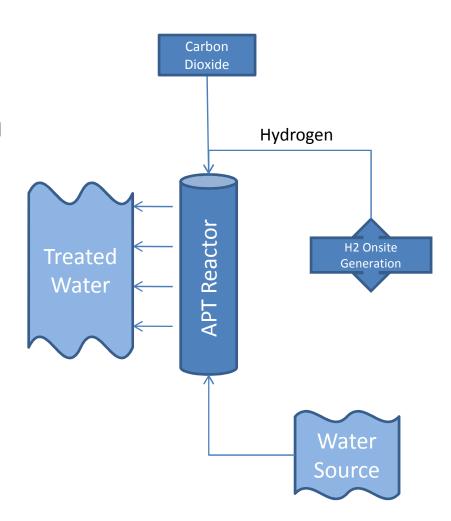
Hydrogen is either generated or delivered on site

Carbon Dioxide is delivered on site and used to control pH

Carbon Dioxide & Hydrogen are fed to the ARoNite Reactor creating the optimum environment for the biofilm

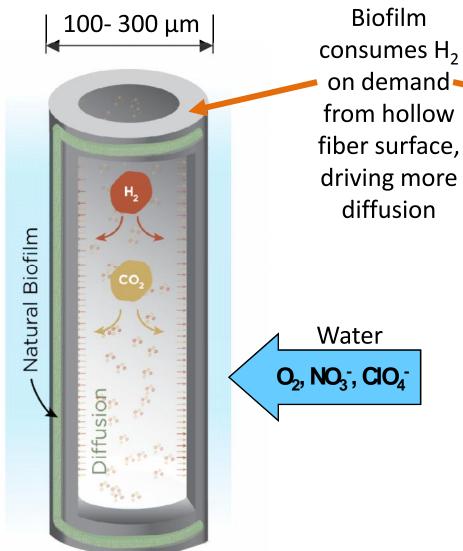
Contaminated water is fed to the ARo Reactor allowing the biofilm to grow and reduce the target contaminant from the water

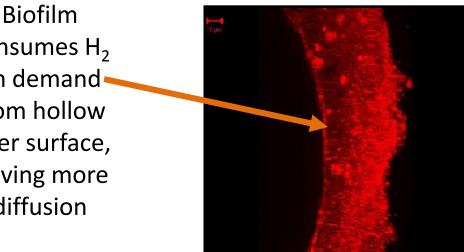
Treated water is filtered and disinfected using conventional technologies before discharge to distribution system



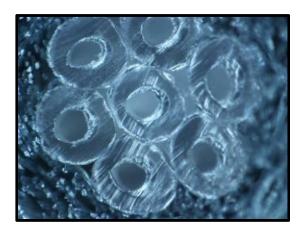


Biofilm supported on a bubble-less gas-transfer fiber



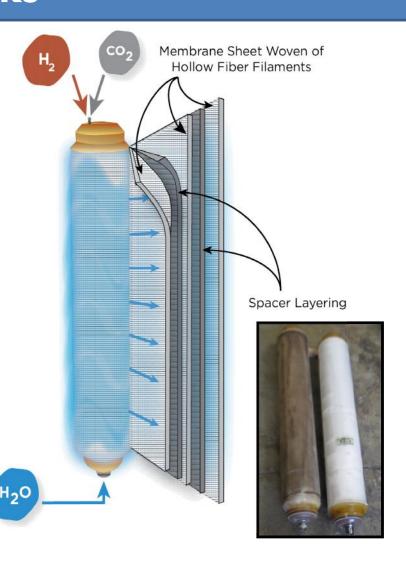


Polypropylene Hollow Fiber Membrane



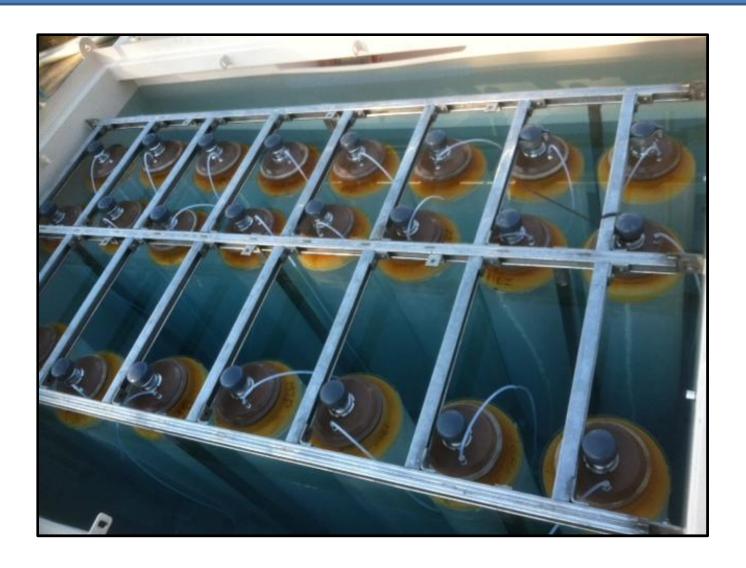
How the ARoNite Reactor Works

- Naturally occurring biofilm grows on the surface of a gas diffusion membrane sheet woven of proprietary hollow fibers
- Several of these sheets are spiral wound around a water feed tube with a water channel spaced between the sheets
- Hydrogen and Carbon Dioxide are fed to the lumen of the hollow fibers
- Water passes between the sheets making contact with the biofilm
- Nitrate is reduced to Nitrogen and Water
- Over time, cells fall off into water and are filtered
- Automated purge cycle prevents fouling





View of the modules in operation





ARoNite Projects – Several Years in Development

| Location | Contaminant | Dates | System configuration | Significant Outcome |
|----------------------|--|-----------------|----------------------|---|
| La Puente, CA | Groundwater ClO ₄ - | ~2003 | Pilot module | AwwaRF Report by MWH, early system design info. |
| Modesto (Grayson) | Groundwater NO ₃ | 9/06 – 6/11 | Pilot module | Multiple fiber and module construction improvements, CDPH data collected |
| Lake Arrowhead | Tertiary effluent NO ₃ - | 3/07-11/07 | Pilot module | WateReuse Report by Trussell |
| San Bernardino | Groundwater NO ₃ -, ClO ₄ - | 3/08 - 1/09 | Pilot module | Flow maldistribution limit performance, ESTCP with CDM reauthorized |
| Glendale, AZ | Groundwater NO ₃ - | 4/08 - 2/09 | Pilot module | WRF Report by CH2MHill, positive comparison to IX and heterotrophic systems |
| Rancho Cordova | Groundwater ClO ₄ - | 9/08 - 11/10 | Pilot module | Successfully treat 14 ppm to <4 ppb |
| Rancho Cordova | Groundwater ClO ₄ - | 10/08 - 11/10 | Commercial module | Develop and test larger modules |
| Ojai, CA | Tertiary effluent NO ₃ - | 2/10 - 12/10 | Commercial module | Tested multitude of large modules in one system |
| Rialto, CA | Groundwater NO ₃ -, ClO ₄ - | 5/11 - 2/12 | Commercial module | ESTCP project with CDM based on improvements in commercial module |
| Burbank, CA | Groundwater NO ₃ -, Cr(VI) | 6/11 - 11/12 | Commercial module | Tested 5 to 50 ppb Cr(VI) removal to ND |
| Rancho Cucamonga | Groundwater NO ₃ - | 11/11 - current | Commercial module | 1 St commercial system for biological nitrate removal |

ARoNite Case Study: City of Modesto

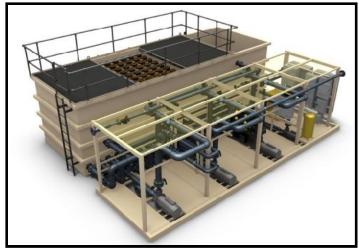
- Sampling and analysis protocol developed w/CDPH for continuous 30day test
- October 29, 2008, to December 1, 2008
- Positive results on all analyses – met DW standards

| Analyte averages | Inlet | Final Product |
|-------------------------|-------|---------------|
| Nitrate-N (mgN/L) | 14.1 | 0.3 |
| Nitrite-N (mgN/L) | <0.01 | <0.01 |
| Chromium (µg/L) (total) | 18.3 | 3.5 |
| Selenium (µg/L) | 10.5 | 6.5 |
| Copper (µg/L) | 9.5 | <2 |

Led to CDPH draft conditions and a commercial demonstration at a specific site for later operation



ARoNite Installation Cucamonga Valley Water District







Project Details:

Drinking Water Well #23 Water-by-the-Gallon (DBOOM) Denitrification

- CVWD has 12 wells shut down out of 30 for nitrates
- All high in nitrate, well over MCL
- Target allowed nitrate <31 ppm
- Two step contract
 - Step 1: Start up and run 125 gpm
 - Step 2: Expand plant to 650 gpm,
- Plant construction; Aug-October, started up Nov 2011
- CDPH testing protocols defined and completed
- CDPH Conditional Acceptance July 2013





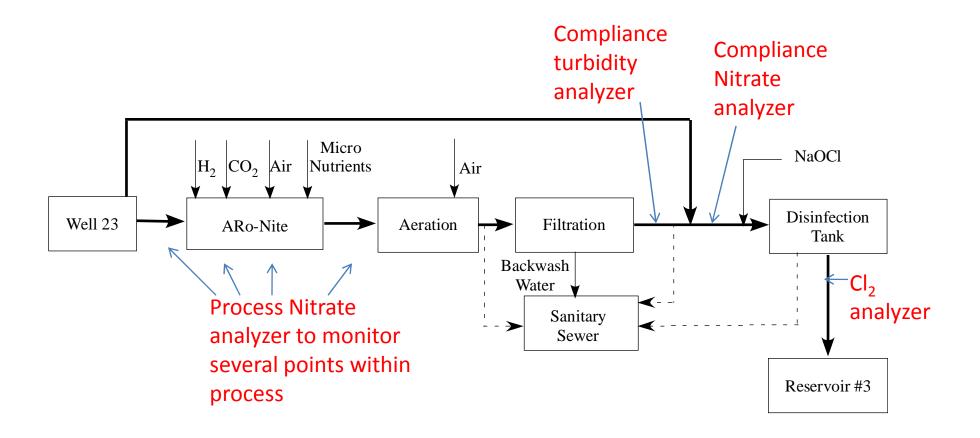






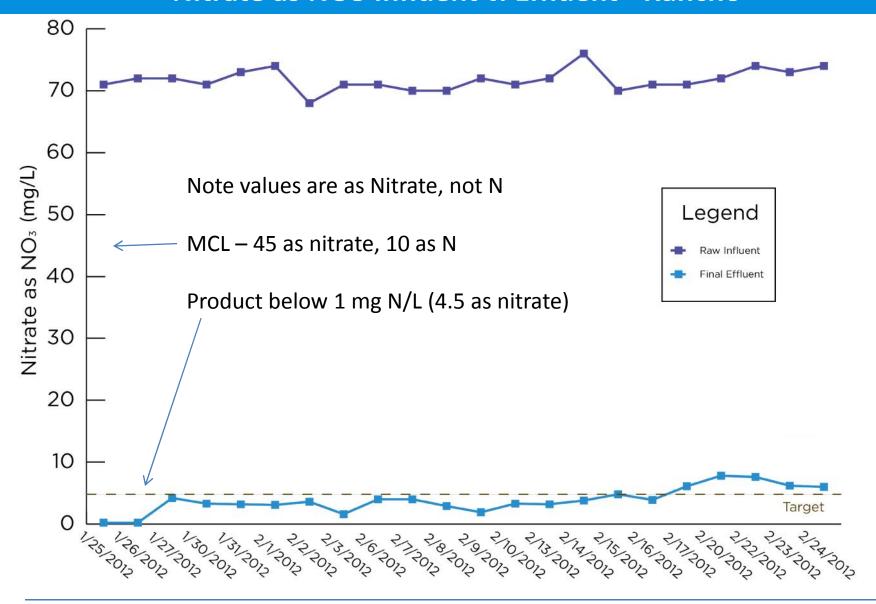


ARoNite Process Overview and Monitoring Points

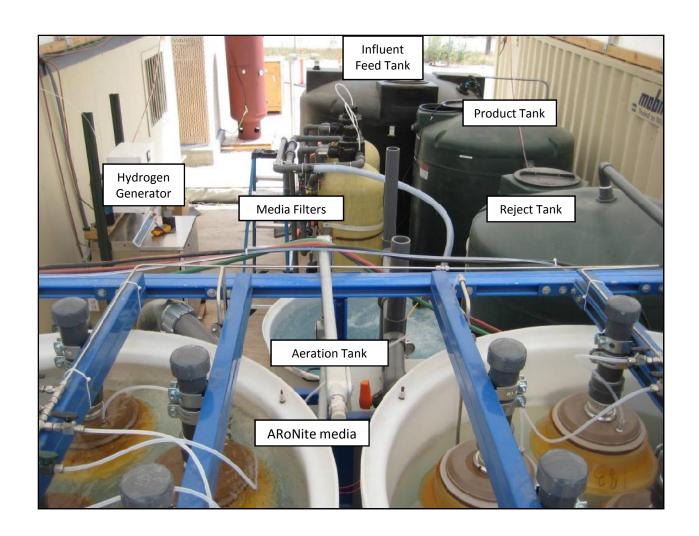




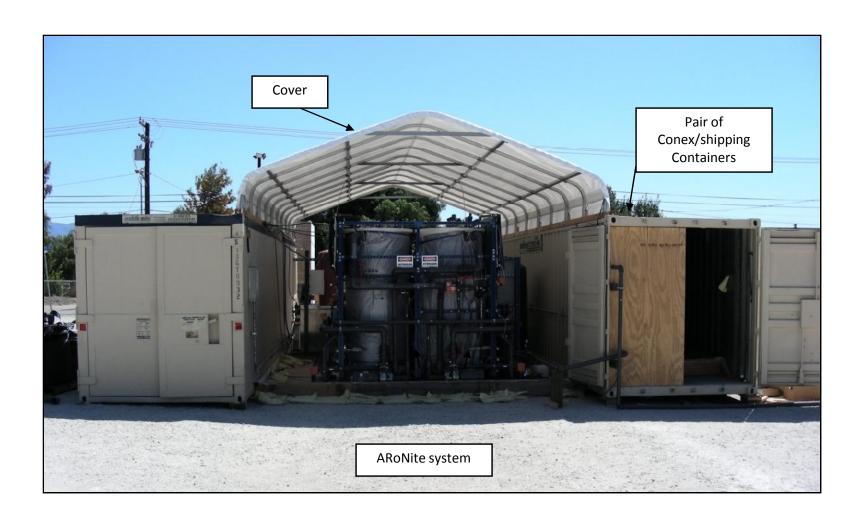
Nitrate as NO3 Influent v. Effluent - Rancho



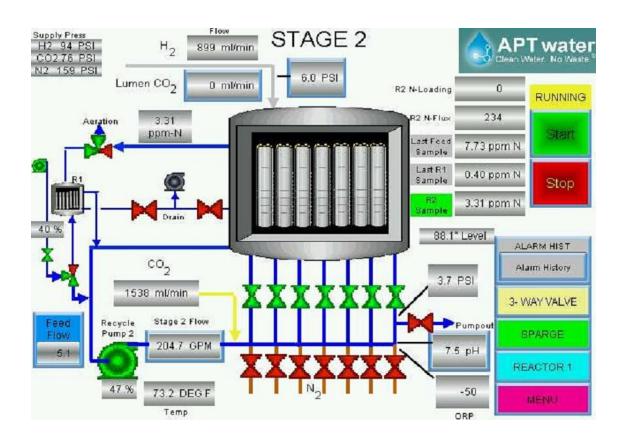
Small System Example



Small System Example



Ready and configured for data logging, remote operation, alarm notification with text/email, video surveillance over cell and internet



Indicative Costing

- Required instrumentation and controls, base system are majority of system independent of 1-50 gpm flow
- Capital range upper 100's to 500K
- O&M consumables
 - Primarily electricity with only CO₂, bleach, filter coagulant delivered.
 - Above approx. \$10-30K/yr, \$700-1000/MGal

What to walk away with

- Utilizes naturally-occurring indigenous bacteria no seeding required
- Very low biomass compared to carbon based system
- Adds no organic residual, no dosing challenges
- Self regulated demand of hydrogen
- Hydrogen can be generated on-site as needed
- Meets and exceeds state and federal drinking water standards for drinking water
- NSF-61 certified
- CDPH acceptance for drinking water applications
- No brine or concentrated waste as Nitrate is destroyed versus concentrated
- Remote monitoring, troubleshooting and control of equipment

Safe Drinking Water



Thanks for your Time and Interest

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